LOSSES OF MERCURY IN TOXICOLOGICAL ANALYSES

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THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMISTRY

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1922

1922
#995

UNIVERSITY OF ILLINOIS

May 25 1922

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DEGREE OF Bachelor of Science in Chemistry

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ACKNOWLEDGEMENT

I take this opportunity to thank Dr.Beal for the suggestion of this problem,and for his sympathetic supervision and guidance in working it out. His friendly suggestions and personal interest have been a source of inspiration to me throughout the work,and if anything of importance has been brought out in this work,it is largely due to the above facts.

LOSSES OF MERCURY IN TOXICOLOGICAL ANALYSES

I.INTRODUCTION

1.-PURPOSE

The purpose of this investigation has been the study and comparison of the three principal methods for the decomposition of organic tissues in the toxicological determination of mercury, in order to determine which of the various methods now known and used,will recover the greatest amount of mercury from organic tissue.

2.NATURE OF THE PROBLEM

It is a well known fact that mercury salts together with other salts,such as arsenic,are quite volatile,and it is due partly to this fact that no method is now known which will recover all of a given quantity of mercury in a toxicological analysis. It is very important inaa toxicological investigation to know the exact quantity of mercury which has been administered to cause the death of the person in question. Proof that a sufficient quantity of poison has been given to cause death constitutes the chief evidence in legal cases. Therefore it is necessary,in toxicological analyses, to know how much mercury is lost in the composition of the organic matter and the subsequent determination of the poison.

3.-HISTORICAL

The methods used for the toxicological determination of mercury are comparatively few in number. The chief object in all of the methods is the complete destruction of the organic material. This

is necessary in order to free the mercury from organic substances, chiefly the albuminoids. Mercury forms a complex salt with albuminous substances present in protein material, and this must be broken before the mercury will go into solution.

I. FRESENIUS & VON BABO METHOD (8)

Fresenius and von Babo worked out a method for the determination of arsenic which was published in 1844. This has been adapted for the toxicological analysis of all metallic poisons including mercury. In this method the decomposition is carried out by the action of nascent chlorine upon the organic tissue. The chlorine is generated by the action of hydrochloric acid on potassium chlorate, both of which are added directly to the tissue, which has been chopped finely and diluted with a little water. The reaction takes place best when heated at the temperature of the steam bath. The decomposition requires several hours. The liquid is filtered off and the mercury precipitated with hydrogen sulphide. The mercury may then be determined by any suitable method.

II. GAUTIER'S METHOD (1)

Gautier worked out a method for the toxicological determination of arsenic which was published in 1875. This method of decomposition consists of oxidizing the material with concentrated nitric and sulphuric acid at rather high temperatures. To 100 grams of the material 30-60 grams of pure nitric acid is added. Then one gram of sulphuric acid is put in and the mixture heated until liquification is produced. It is then removed from the heat and 8-10 grams of sulphuric acid added. This is then heated again (taking care not to carbonize the mass) and taken from the source of heat. Nitric acid is then poured over the material a little at a time until up

on heating to a point where dense white vapors come off, there is left in the casserole a brown thick liquid carbonizable at the boiling temperature of sulphuric acid. When the nitric acid produces scarcely any further oxidation, the acid is driven off by heat, the material allowed to cool, a little sulphuric acid added, and the small quantity of residual liquid poured into 600 or 700 c.c. of distilled water. The arsenic or mercury can then be precipitated in the usual way and determined. This method was worked out from Orfila's[2] proceedure, published in 1853, and Filhol's[3] work published in 1848.

III. CHITTENDEN & DONALDSON[4] METHOD.

Chittenden and Donaldson while endeavoring to find a more suitable and accurate method for the toxicological determination of arsenic, worked out a modification of Gautier's[1] proceedure, which was published in 1880. They claim its advantage over the method of Gautier because the decomposition is carried out at lower temperatures. In this proceedure the sulphuric acid is not added until the nitric acid has practically reduced the organic material to a liquid. This liquid is then watched closely, and when it becomes thick and assumes an orange shade, the casserole is taken from the hot plate and 3 c.c. of concentrated sulphuric acid added while stirring constantly. The addition of the sulphuric acid to this residue rich in nitrous compounds causes nitrous fumes to be given off copiously, followed by dense white fumes. The residue is carbonized to a black sticky mass or else a dry char. After heating some more and adding a few c.c, of nitric acid, in order to more completely destroy the organic material, and prevent formation of sulphides, the casserole is removed from the heat. A hard carbonaceous mass free from nitric acid is the result. The arsenic may then be dis-

solved out with successive portions of warm water, and determined as in the previous method.

(6)

IV.HARKINS AND SWAIN METHOD.

Just as the Chittenden and Donaldson method is a modification of Gautier's (1) so may Harkins's and Swain's proceedure be called a modified Chittenden-Donaldson method. The proccedure differs from Chittendon - Donaldson (4) method in that the mixture is the casserole is removed from the heat just as soon as it has been completely reduced to a liquid. After cooling the liquid, about 30c.c. of concentrated sulphuric acid is added and the casserole heated. Great quantities of nitrous fumes are driven off. When the liquid begins to get brown, nitric acid is added from a dropping funnel, in sufficient quantity to maintain the brown color, and prevent any further darkening. This is kept up until the liquid in the vessel no longer changes color. This thick liquid is now free from nitric acid and a great deal of sulphuric acid is also gone. It is diluted and evaporated to a smaller volume and is then ready for the precipitation of mercury.

All of the above methods were used by the authors for determination of arsenic, but have since been adapted for mercury and other metallic poisons.

II.EXPERIMENTAL

1.-MATERIAL

The material used in this work was dried blood. This dried blood was of very low moisture content, so that twenty five grams of the dried material was taken to equal one hundred grams of tissue. In all determinations this amount was used.

2.PREPARATION OF MATERIAL

The dried blood after being weighed out roughly, was put

into a vessel and enough water added to form a pasty or soupy mass. This was then allowed to stand, in general, about an hour in order that the blood might become softened and brought to a state as nearly resembling the original condition as possible.

Mercuric chloride was chosen as the most suitable mercury compound, since it is the most common of the mercury poisons to be dealt with in toxicological work. By adding the mercuric chloride to the blood mixture in the form of a solution in all cases we felt that we had a fair duplication of toxicological conditions. This solution was of known titer, and was retitrated frequently to detect any change in strength which might take place from time to time. The solution was made up of approximately tenth normal strength, in order to facilitate the addition of mercury in small amounts to the material.

After adding the mercuric chloride to the material, the blood mixture was allowed to stand forty eight hours. This gave opportunity for the mercury to thoroughly impregnate the organic matter, and reach a condition somewhat similar to that existing in the animal body, when death and possibly burial follows administration of the poison. It is supposed that mercury forms a mercury albuminoid in the tissue. It is due to this fact that organic material must be destroyed before mercury can be determined. After standing this length of time the decomposition may be started according to the method selected.

1.-WORK ON THE FRESENIUS-VON BABO[8] METHOD.

In carrying out the decomposition by this method it was decided to vary the proceedure. One set of decompositions was carried out in an open flask, and another set using a reflux condenser. By using the condenser, any mercury which might volatilize with steam would be returned to the flask and thus be determined. By comparing

the results of the two differently conducted decompositions,the amount of mercury lost by volatilization might be easily found.

Following the proceedure of Fresenius-Von Babo thirty c.c. of concentrated hydrochloric acid was added to the mixture followed by from one to two grams of potassium chlorate. The Kjeldahl flask containing this mexture was then put on the water bath. The nascent chlorine coming into contact with the organic material soon began to act. After a short time,when the potassium chlorate was used up,more was gradually added(about .2 to .3 gram at a time). Generally,this amount added about every five to ten minnutes kept an even flow of chlorine. The mixture soon began to get lighter in color. Shaking the flask after addition of each portion of potassium chlorate accelerated the decomposition noticeably,by bringing the chlorine into contact with the tissue. The end of the decomposition was indicated when the liquid assumed a light straw color, and did not darken on standing,or upon further heating. A little dilute sulphuric acid was then added to precipitate any possible barium or lead and the supernatant liquid was filtered off. The mercury was precipitated from the solution with hydrogen sulphide, after expelling all free chlorine. The gas was allowed to buble through the liquid for one and one half hours while hot. The liquid was then removed from the water bath and the gas allowed to run until the flask cooled. The liquid containing the mercury sulphide precipitate was corked and allowed to stand for one day. If at the end of that time an odor of hydrogen sulphide was noticeable in the flask,the precipitate was filtered off. Otherwise,more hydrogen sulphide was passed into the liquid. The black residue of mercury sulphides was then dissolved in nitric acid with a few drops of hydrochloric acid and the resulting solution diluted and filtered. This filtrate containing the mercury was then ready for determination.

The determination was carried out volumetrically, using the method of Bauer.(5) Following his proceedure the solution was made alkaline with ammonia, and a standard solution of potassium cyanide added to the mercuric solution. Five c.c. of potassium iodide was added as an indicator and the excess of potassium cyanide titrated with standard $\frac{N}{10}$ silver nitrate. Each c.c. of $\frac{N}{10}$ silver nitrate is equivalent to .02006 grams of mercury. The potassium cyanide solution was previously titrated against the $\frac{N}{10}$ silver nitrate solution, so that the value of the potassium cyanide solution per c.c. was known.

In carrying out the duplicate decomposition with the reflux condenser the potassium chlorate was added by loosening the condenser from the flask and dropping in the potassium chlorate. It was found in running the two sets of decompositions that the liquid in the flask bearing the reflux condenser always reached the final stage before the open flask. Also, less potassium chlorate and acid were necessary than with the open flask, in order to produce the final stage of decomposition. No difficulty was experienced in carrying out the decompositions according to this method. However, some of the organic matter could not be destroyed by the action of the chlorine. It always remained in the bottom of the flask in the form of a white mealy substance. It was easily filtered off, leaving a clear liquid. The most important source of error seemed to be in not allowing enough time for complete decomposition. If the flask was removed before it had reached the right stage, difficulty follow-in precipitating the mercury from the solution. The writer experienced this trouble early in the proceedure. Stringy, slimy compounds were thrown down with the mercury when hydrogen sulphide was passed into the solution. These were later dissolved by the nitric and hy-

drochloric acids,with the result that when the ammonia and potassium iodide were added for titration,a murky precipitate clowded the solution and made titration impossible. It was not always possible to filter this off,and even iff possible,presented the objection of removing some of the mercury with the other substances. Therefore, the best way seemed to be to avoid this by thoroughly decomposing the organic matter in the beginning,until the permanent straw color appeared. The time for each decomposition was noted and recorded.

2.CHITTENDEN AND DONALDSON METHOD.

The work on this method was confined to a few decompositions only,since the nature of the proceedure suggested great,if not total losses of mercury.

Following their proceedure,23 c.c. of pure concentrated nitric acid is added to the blood mexture containing the mercury. The mixture contained in a casserole of 600c.c. capacity is then heated on a hot plate with occasional stirring. The temperature as mentioned by the authors of this method is 150-160 degrees centigrade,but with the blood this temperature was not attained. This would seem to be favorable. Keeping at this temperature,the mass swells,thicken,and changes color. At first a dark brown,it changes slowly to a light yellow. It then becomes a liquid. This is heated 1 1/2 to 2 hours until it takes on an orange color,or deep yellow shade. At this point,the casserole is removed from the plate and 3 c.c. of concentrated sulphuric acid added while stirring vigorously. The mixture thickens and gives off nitrous fumes copiously, immediately followed by dense white fumes of sulphur trioxide. The residue in the dish is changed into a black sticky mass or else a dry carbonaceous mass. The dish is again placed on the plate and heated for a few minutes. Then 8 c.c. of nitric acid is added,drop

by drop,in order to more completely destroy the organic matter,and precent the formation of the organic sulphide. After this addition, the casserole is again heated for 15 minutes,after which the cold carbonaceous mass is treated with hot water in successive portions, in order to extract the mercuric sulphate. This water is then evaporated and the mercury taken up from the residue with concentrated hydrochloric acid. This extract is diluted with water and the mercury sulphide precipitated. The precipitate may then be dissolved and titrated as in the first method.

In following out the above method,the temperatures as stated by the authors exceed those reached in using the blood mixture. Since the blood mixture is more fluid than solid tissue the temperature would naturally be lower in this case. In extracting the mercury salt from the carbonaceous residue,the water was left in contact with the mass for 24 hours in order to insure complete extraction. No difficulties were encountered in carrying out the proceedure,but it was necessary to watch the mixture very closely before adding the sulphuric acid. It was difficult to detect the change in color because of the red nitrous fumes,which were given off. It was necessary to exercise care in adding the sulphuric acid, in order to prevent any loss by spattering. Affew drops were added at a time and the mixture stirred vigorously during addition.

3.-WORK ON HARKINS AND SWAIN METHOD.

In carrying out this proceedure 500 c.c. casseroles were used as the vessels. four determinations were carried out together. This number was found to be convenient,in saving time. One decomposition was started and carried to the end of the first stage. It was allowed to heat while another was started.

One hundred c.c. of concentrated nitric acid was added to the blood mixture and placed on the hot plate. The mixture begain to swell and required constant stirring to avoid the overrunning of the dish. It changed color from a dark brown to a light yellow. Here the swelling subsided and after a little while became a liquid. This liquid was then allowed to heat for half an hour,while another decomposition was started. The rich red liquid was then removed and allowed to cool,after which 30 c.c. of concentrated sulphuric acid was added. The casserole was again heated on the hot plate. Great volumes of red nitrous fumes came off. This continued for some time, when the liquid begain to assume a brown color. Here,nitric acid was added,drop by drop,just enough to prevent the darkening of the liquid. This was continued until the thick liquid no longer changed color. The mixture was heated a little longer to drive off some of the thick white sulphur trioxide fumes,in the meanwhile,adding nitric acid occassionally. The casserole was then removed from the heat and allowed to cool,after which the residue was diluted and reevaporated to a smaller volume,in order to eliminate any nitrous fumes. This solution was then filtered and the mercury precipitated from it in the usual way,and determined. No difficulty was encountered in the proceedure. The organic material was completely destroyed and good clear solutions were obtained for the titration. In running the four decompositions in the manner described it required the entire attention of the writer,and although the work was carried out under the hood the fumes from the dishes were very disagreeable. The time occuppied was about one hour.

4.- NEW METHOD TRIED.

It was decided to modify the Harkins-Swain method in such a way as to eliminate the great losses of mercury which neces-

sarily take place at the higher temperatures produced by adding the sulphuric acid. The first part of the proceedure using the nitric acid was carried out as before,and the mass reduced to a liquid. After cooling the mixture it was transferrdd from the casserole to an 800 c.c. Kjeldahl flask which was fitted with a reflux condenser. The mixture was then heated with a bunsen burner to boiling,after having added the sulphuric acid,for about an hour and one half. The red nitrous fumes were driven off from the top of the condenser, while the rest of the material which volatilized was condensed and returned to the flask. Some carbonization was noticeable as the heating was continued,but the liquid remained a light color. The black flakes of carbon remained on top of the clear liquid. After most of the nitric acid had been driven off,as was shown by the fact that scarcely any red fumes came from the top of the condenser,the flask was removed from the heat and allowed to cool. The clear liquid was filtered off and diluted. Since the solution contained mostly dilute sulphuric acid,the passing in of hydrogen sulphide gave rise to a light yellow precipitate of sulphur. This copious precipitate of sulphur obscured the precipitate of mercury sulphide for a few minutes,but it appearred presently on the surface of the solution. After precipitation was complete the sulphur and mercuric sulphide were filtered off. The mercuric sulphide was then dissolved with nitric and hydrochloric as previously and titrated.

It was thought at first that the sulphur might interfere in dissolving the mercury sulphide,but the metal was easily separated and the sulphur left undissolved. The solution finally obtained for titration gave no trouble,as it remained clear after adding the various solutions needed for titration. Although this method occuppied a little more time,no disagreeable odors were experienced,

and it required less attention. Any mercury which might have volatilizedwas immediately condensed and carried back into the flask by the water which was being returned to the flask from the condenser. Therefore,any loss of mercury caused by volatilization must have occurred in the first part of the process when the decomposition was started with the nitric acid.

5.-METHOD WITH CONCENTRATED SULPHURIC ACID AND PERCHLORIC ACID.

It was decided to investigate the action of concentrated sulphuric acid and perchloric acid on organic tissue in the hope that this might prove a means of breaking up the tissue.

Therefor fifty c.c. of concentrated sulphuric acid was added to the blood mixture and heated on the water bath. A seventy percent perchloric acid was obtained and a few c.c. added at a time, but no reaction resulted. The flask was then raised to a higher temperature,and finally to the boiling point of the sulphuric acid, and the perchloric acid was again tried. No results followed and the method was abandoned as unsuccessfull.

III.RESULTS AND DISCUSSION

TABLE I

Determinations by Fresenius-VonBabo Method

Open Flask

	Theor.Hg.	Time(hrs)	Det.Hg.	Hg.loss	Hg.% loss.
1.	.2316 Gr.	5	.1426 Gr.	.0890 Gr.	38.4
2.	,3088	4	.2505	.0583	15.6
3.	.3088	5	.2062	.1026	33.2
4.	.3860	4	.3348	.0512	13.2
5.	.5404	4 1/2	.4239	.1165	21.2
6.	.6780	3 1/2	.4580	.2200	32.4
7.	.7540	4	.6326	.1214	16.1

Condenser Flask

	Theor.Hg	Time(hrs)	Det.Hg	Hg.loss	Hg.% loss.
1.	.2316	4	.1174 Gr.	.1142 Gr.	49.3
2.	.3088	3	.2060	.1028	33.2
3.	.3088	4	.2013	.1075	34.8
4.	.3860	3	.2736	.1124	29.1
5.	.5404	3	.3906	.1498	27.7
6.	.6780	2 1/2	.4136	.2644	39.0
7.	.7540	3	.6076	.1464	19.9

Table I shows the comparative results of the two variations of the Freseniu-Von Babo Method. The most surprising thing about these results in the fact that the open flask decomposition gave the smallest loss of mercury in every single case. This seems to indicate that the losses were not caused by volatilization,to any extent. It was decided to investigate the condenser to determine

if any volatilized mercury could have sublimed there. It was rinsed thoroughly with water and the washings titrated with a negative result. The only way left, then, to explain the difference in the losses from the same amounts of mercury under the two differently conducted decompositions in in the time of decomposition. The table shows that the open flask decomposition required about an hour longer in each case, to reach the right color. The chlorine will not break up all of the organic material. There was always a white mealy residue left in the bottom of the flask. This fatty material resists the action of the chlorine, so that the losses in mercury may correspond to that held by this solid residue. If this last fatty material could be broken up by some other means and added to the recovered mercury, very little would be lost. The only objection here would be the length of time required to make a determination.

From the condenser flask the mercury losses increase in weight as the amount of mercury added is increased. The percentage of mercury lost steadily decreases as larger quantities of mercury are determined. In comparing this with the open flask figures, there is a wide variation in the percent of mercury lost. However, if the first and last percents are taken, it corresponds very nicely to the condenser flask figures. The mercury losses show a general increase as the quantity of mercury is increased.

TABLE II

Chittenden and Donaldson Method

	Theor.Hg	Det.Hg.	Hg.loss	Hg.% loss
1.	.3016Gr.	.0206 Gr.	.2810 Gr.	93.2
2.	.5278	.0186	.5092	96.4
3.	.7540	.0332	.7208	95.1

The extreme accuracy claimed for this method by its authors is not verified by these figures. Almost all of the mercury was lost by volatilization at the higher temperature used for carbonization. Not enough determinations were run to ascertain in what order the losses would follow, but the few in Table II show great irregularity, depending upon the variations in each decomposition. The best thing that can be said for this method is that it requires only a short time to complete a decomposition.

TABLE III

Harkins and Swain Method

	Theor.Hg.	Det.Hg.	Hg.loss	Hg.% loss
1.	.2262 Gr.	.0470 Gr.	.1792 Gr.	79.2
2.	.3770	.0540	.3230	85.7
3.	.4524	.0860	.3664	80.9
4.	.5278	.1097	.4181	79.2
5.	.6036	.0560	.5476	90.7
6.	.6786	.0320	.6466	95.2
7.	.7540	.1360	.6180	81.9
			Av.	84.6

The results in Table III show an average loss of mercury to the extent of 84.6 percent of the theoretical. These results show that as the amount of mercury determined increases, the losses increase proportionately, and the percentage loss varies from 80 to 85 in most cases. This a much lower loss than the Chittendon and Donaldson Method, but that was expected since the temperature used here was not so high.

TABLE IV.

New Method tried.Modified Harkins and Swain

	Theor.Hg.	Det.Hg	Hg.loss	Hg.% loss.
1.	.3016 Gr.	.0930 Gr.	.2080 Gr.	68.9
2.	.4524	.3194	.1330	29.4
3.	.6016	.4468	.1548	25.7

It can be seen from the data in Table IV that the losses of mercury are much less in this method than in the Harkins and Swain Method. The losses increase as the amount of mercury added is increases,while the percentages of loss show a gradual decrease. Limited time permitted only the three determinations,but it is thought that if intermediate quantities of mercury were used,the interpretation would be the same as shown by the above data. Determination number one seems to show rather too high percentage loss in proportion to numbers two and three. The chief objection which might be advanced against this method is the length of time necessary for refluxing the mixture,but inasmuch as it requires no attention,the time is not really important. The advantage over the Harkins and Swain Method is that no disagreeable fumes have to be encountered. The chief advantage is ,of course,the reduced amount of mercury which is lost by volatilization. The sulphur which is thrown down with the mercury on precipitation is really not objectionable,since the mercury is easily dissolved out of the sulphur mass.

TABLE V.

Comparison of Methods

Method	Av.Theor.Hg.	Av.Det.Hg.	Av.Hg.loss	Av.% loss
1.Fresenius-Babo	.4576 Gr.	.3498 Gr.	.1084 Gr.	24.3
2.Chitt'n-Don'son	.5278	.0261	.5017	95.1
3.Harkins-Swain	.5170	.0744	.4426	84.6
4.New Method	.4519	.2864	.1655	41.3

Table V is given for convenience in comparing the general results of the four methods worked on. The average percent loss gives a pretty fair estimate of the value and accuracy of the methods,except in the case of number four. The first determination carried out with this method gave,for some reason or other,quite a high mercury loss. This result was too high to be consistant with the two later determinations as is shown by Table IV. As a consequence, this one high loss inflates the average percentage loss much higher than it really should be. If we discard this one high loss,the new method compares very favorably with the Fresenius-Von Babo Method. Of course,the averages given apply to quantities of mercury bettween .25 to .75 gram. It is the belief of the writer that the new method as described can be improved and developed where much lower losses of mercury will occurr.

IV. SUMMARY AND CONCLUSIONS

I. The four possible methods for the toxicological determination of mercury have been reviewed and the three most promising ones investigated.

II. Losses of mercury in the Fresenius-Von Babo method are not due to volatilization to any extent, but to the undecomposed tissue which is filtered off after decomposition.

III. The Chittenden-Donaldson method uses too high a temperature for decomposition, thereby volatilizing the greatest percent of the mercury(95%).

IV. The Harkins-Swain method uses a lower temperature but the decom-
p position temperature is high enough to allow great losses of mercury. This makes it unsuitable for determination of small quantities of mercury

V. Disagreeable fumes are encountered in this method.

VI. The new method tried gave much smaller mercury losses than either the Chittenden-Donaldson or Harkins-Swain methods.

VII. The new method compares very favorably with the Fresenius-Von Babo method

VIII. It can be developed so as to give much lower losses.

IX. Of the four known methods Fresenius-Von Babo method gives the smallest losses, and seems to be the most suitable for determining small quantities of mercury in organic tissue. It is better because it

1. Uses a comparatively low temperature.
2. Gives no disagreeable odors.
3. Uses only one acid.

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